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**Title of the Invention: Polyethylene Naphthalate for Bottles**

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(21) Application No.:	6-50250	(71) Applicant:	000003001	
(22) Date of Filing:	March 22, 1994		Teijin Ltd. 6-7, 1-chome Minami-hon-machi, Chuo-ku, Osaka-shi, Osaka-fu	
		(72) Inventor:	Hironori Nagano c/o Teijin Ltd., Matsuyama Office 77 Kita-yoshida-cho, Matsuyama-shi, Ehime-ken	
		(74) Agent:	Sumihiro Maeda, Patent Attorney	

**(54) [Title of the Invention]**

Polyethylene Naphthalate for Bottles

**(57) [Summary]**

**[Object]** To develop polyethylene naphthalate to be used for bottles that has good heat stability and excellent hue and transparency.

**[Means of Achievement]** Polyethylene naphthalate with high transparency in a specific polymer solution by containing Mn, P, and Sb compounds in quantities that satisfy the following equations as the catalyst.

$$0.7 \text{ mol} \leq \text{Mn} \leq 1.7 \text{ mol}$$

$$0.5 \leq \text{Mn/P} \leq 1.2$$

$$1.0 \text{ mol} \leq \text{Sb} \leq 3.0 \text{ mol}$$

**[Claims]**

**[Claim 1]** Polyethylene naphthalate for bottles that is a polyester with an acid component consisting mainly of naphthalene dicarboxylic acid and a glycol component consisting mainly of

ethylene glycol, that contains as catalysts a manganese compound, phosphorus compound, and antimony compound in the quantities shown by the following numerical formulas (1) through (3), and, when dissolved in a concentration of 10 mg/mL in a 2/3 hexafluoroisopropanol/chloroform mixed solvent, the polymer has a transmittance ( $T_{400}$ ) at a wavelength of 400 nm of 95%/cm or higher, and the difference ( $\Delta T$ ) between this transmittance ( $T_{400}$ ) and the transmittance ( $T_{420}$ ) at a wavelength of 420 nm is 3%/cm or less.

$0.7 \text{ mol} \leq \text{Mn} \leq 1.7 \text{ mol}$ .....(1)

$0.5 \leq \text{Mn}/\text{P} \leq 1.2$ .....(2)

$1.0 \text{ mol} \leq \text{Sb} \leq 3.0 \text{ mol}$ .....(3)

(each metal element in the equations shows the number of moles of metal per  $10^6$  g of acid component)

**[Claim 2]** The polyethylene naphthalate of Claim 1 wherein the antimony compound is antimony acetate.

**[Claim 3]** The polyethylene naphthalate of Claim 1 wherein the trunk haze when a bottle is molded (thickness: 0.2 mm) is 1.5% or less.

#### **[Detailed Description of the Invention]**

##### **[0001]**

**[Technological Field of the Invention]** The present invention relates to polyethylene naphthalate. More specifically, it relates to polyethylene naphthalate that has good heat stability, excellent hue, transparency, and gas barrier property, and is useful in molding bottles.

##### **[0002]**

**[Prior Art and Problems to Be Solved by the Invention]** PEN is expected to be useful as a packaging material, especially for bottles and sheet materials, because it has better basic properties such as heat resistance, gas barrier property, and mechanical strength than polyethylene terephthalate (abbreviated hereinafter as PET). Numerous packaging materials have been proposed that use blends of PEN and PET or PEN alone.

**[0003]** Good hue and transparency are generally strongly desired in packaging materials, especially bottles. Even though PEN can basically be reacted using the same catalyst systems as PET, the use of titanium compounds as the catalyst results in severe discoloration and deterioration of the hue during polymerization. Catalysts other than titanium compounds

therefore should be used. Aside from this, PEN undergoes greater whitening than PET during bottle molding, posing a problem from the standpoint of transparency. Subsequent studies on the cause of this interference with transparency found mainly compounds formed of the components used as the catalyst and the polymer components to form a precipitate which leads to optical scattering by its presence within and on the surface of the polymer, thus harming the transparency. Means such as restricting the catalyst to specific types, amounts, and ratios were proposed as means for minimizing the production of this precipitate by the catalyst and such. Even though these catalyst systems certainly improve the transparency of PEN, the hue and heat stability are inadequate, and the effects as regards use in bottles also are not stated.

[0004] With the foregoing in view, the present inventors conducted in-depth studies, and as a result of which discovered that polyethylene naphthalate with good heat stability during bottle molding and excellent transparency and hue as molded goods is obtained when specific types, quantities, and proportions of catalysts are selected and the optical properties of the polymer solution obtained satisfy specific values, and thereby attained the present invention.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]** The present invention is polyethylene naphthalate for bottles that is a polyester with an acid component consisting mainly of naphthalene dicarboxylic acid and a glycol component consisting mainly of ethylene glycol, that contains as catalysts a manganese compound, phosphorus compound, and antimony compound in the quantities shown by the following numerical formulas (1) through (3), and, when dissolved in a concentration of 10 mg/mL in a 2/3 hexafluoroisopropanol/chloroform mixed solvent, the polymer has a transmittance ( $T_{400}$ ) at a wavelength of 400 nm of 95%/cm or higher, and the difference ( $\Delta T$ ) between this transmittance ( $T_{400}$ ) and the transmittance ( $T_{420}$ ) at a wavelength of 420 nm is 3%/cm or less.

0.7 mol  $\leq$  Mn  $\leq$  1.7 mol.....(1)

(each metal element in the equations shows the number of moles of metal per  $10^6$  g of acid component.

The present invention is explained below.

[0006] The term "mainly" means 70 mol% or more, and preferably 80 mol% or more. Therefore, it may contain less than 30 mol% of other components as a copolymer or mixture.

[0007] The term "naphthalene dicarboxylic acid" in the present invention means mainly 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, and ester-forming derivatives thereof. Part (less than 30 mol%) may be substituted by another dicarboxylic acid, e.g., oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid, dodecanedicarboxylic acid, and other such aliphatic dicarboxylic acids; terephthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, diphenoxymethane-4, 4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, diphenylether-4,4'-dicarboxylic acid, and other such aromatic dicarboxylic acids; hexahydroterephthalic acid, decalinedicarboxylic acid, terinalinedicarboxylic [sic] acid, and other such alicyclic dicarboxylic acids; glycolic acid, p-oxybenzoic acid, and other such oxy acids. Examples of ester-forming derivatives of the acid component include lower alkyl esters, phenyl esters, and acid anhydrides.

[0008] The term "glycol component" means mainly ethylene glycol. Part (less than 30 mol%) may be substituted by another glycol, e.g., tetramethylene glycol, propylene glycol, 1,3-butanediol, neopentyl glycol, and other such aliphatic siols [sic; diols]; cyclohexanediethanol, tricyclodecanediethanol, and other such alicyclic diols; bisphenol A, bisphenol S, bishydroxyethoxybisphenol A, tetrabromobisphenol A, and other such aromatic diols. Also, as in ordinary polyesters, phosphorus and other such heat stabilizers, hindered phenols and other such antioxidants, benzotriazole, hydroxybenzophenone, cyanoacrylate, and other such ultraviolet absorbers, titanium oxide, carbon black, terazole [sic; tetrazole] blue, and other such pigments, dyes, talc and other such nucleating agents, higher fatty acid salts and other such crystallization accelerators, mold release agents, and the like may be added.

[0009] The present invention also encompasses copolymers of trifunctional or higher functional polycarboxylic acids or polyhydroxy compounds, such as trimellitic acid and pentaerythritol, in quantities of the range where the copolymer is substantially linear, e.g., quantities of 2 mol% or less versus the total acid component.

[0010] The polyethylene naphthalate of the present invention can be produced by a conventional polyester production process. However, transesterification; i.e., production by reacting a lower alkyl ester of naphthalene dicarboxylic acid and ethylene glycol, is preferred. Part (e.g., 20 mol% or less) of the lower alkyl ester of naphthalene dicarboxylic acid in this reaction may be

substituted by another acid component, and part (e.g., 20 mol% or less) of the glycol may be substituted by another glycol component.

[0011] Examples of lower alkyl esters of naphthalene dicarboxylic acid include dimethyl, diethyl, dipropyl, and other such esters. A dimethyl ester is especially preferred.

[0012] In the production of the polyethylene naphthalate of the present invention, a soluble manganese compound is first added to the reaction system to make a total of 0.7-1.7 mol of elemental manganese per  $10^6$  g of the acid component in the reaction of the lower alkyl ester of naphthalene dicarboxylic acid and ethylene glycol, and transesterification is carried out (the term "mol" hereinafter shows the number of moles per  $10^6$  g of acid component). This quantity is preferably 1.0-1.5 mol. If the amount of manganese compound added as transesterification catalyst versus the acid component exceeds the above 1.7 mol, the surface smoothness deteriorates due to the effect of the precipitated particulate caused by catalyst residues when a bottle is molded, resulting in poor transparency of the bottle. On the other hand, if the amount added is less than 0.7 mol, the transesterification reaction alone is inadequate or the subsequent polymerization reaction also slows.

[0013] Next, when the transesterification reaction has substantially been completed, a phosphorus compound is added to inactivate part of the transesterification catalyst. The molar ratio [Mn/P] of phosphorus compound added versus the transesterification catalyst; i.e., the manganese compound, is preferably 0.5-1.2. The ideal range is 0.6-1.1. If this molar ratio is less than 0.5, the surface smoothness deteriorates under the influence of precipitated particles due to the phosphorus catalyst residues when molded into a film. On the other hand, if the molar ratio exceeds 1.2, the activity of the manganese compound not inactivated by the phosphorus compound causes the heat stability of the polyethylene naphthalate to deteriorate, leading to poor hue when molded into a bottle.

[0014] Although the manganese compound used in the present invention is not particularly restricted, oxides, chlorides, carbonates, carboxylates, and the like are preferred. An acetate; i.e., manganese acetate, is especially preferred.

[0015] A polymer is made thereafter by polycondensation of the reaction product. An antimony compound is added to this reaction product as the main catalyst of the polycondensation reaction. The antimony compound may also be added prior to beginning the transesterification reaction. The amount of antimony compound here must be in the range of 1.0-3.0 mol as the amount of

elemental antimony. If the amount added exceeds 3.0 mol, precipitates derived from the antimony compound form defects in the bottle. On the other hand, if the amount added is less than 1.0 mol, the polycondensation reactivity is poor and productivity becomes poor.

[0016] Oxides, chlorides, carbonates, carboxylates, and the like are preferred as the antimony compound used in the present invention. When an acetate; i.e., antimony acetate, is used in particular, fewer precipitated particles are generated in the polymer than by other compounds, and the transparency of the bottle improves.

[0017] Examples of the phosphorus compound include trimethyl phosphate, triethyl phosphate, tri-n-butyl phosphate, and phosphoric acid. Trimethyl phosphate is preferred, but the compound is not limited thereto.

[0018] The polyethylene naphthalate of the present invention must have a transmittance ( $T_{400}$ ) at a wavelength of 400 nm of 95%/cm or higher, preferably 97%/cm or higher, when the polymer is dissolved in a concentration of 10 mg/mL in a 2:3 mixed solvent of hexafluoroisopropanol and chloroform. Furthermore, the difference ( $\Delta T$ ) between this transmittance ( $T_{400}$ ) and the transmittance ( $T_{420}$ ) at a wavelength of 420 nm must be 3%/cm or less.

[0019]  $T_{400}$  and  $\Delta T$  in the present invention are greatly affected by interference such as precipitated particles, catalysts residues, and foreign matter in the polyethylene naphthalate polymer and heat deterioration during polymerization. If  $T_{400}$  is less than 95%/cm or  $\Delta T$  is more than 3%/cm, whitening occurs during flow [sic] stretching and the hue becomes intensely yellow when used to mold bottles.

[0020] The polyethylene naphthalate of the present invention has excellent transparency, hue, and heat stability. It also has a high gas barrier property. It is therefore very useful as a bottle material for juices, soft drinks, carbonated drinks, and the like.

[0021] The method of molding bottles using the polyethylene naphthalate of the present invention is not particularly restricted, and methods used for ordinary PET such as injection blow molding, direct blow molding, and biaxial blow molding can be used. However, if the haze of the bottle molded is high (i.e., is not transparent), the product will be of no value. It is therefore strongly desired that the haze (cloudiness) be no more than 1.5%.

[0022]

**[Working Examples]** The present invention is explained more concretely below through working examples. The present invention, however, shall not be limited to the working examples

as long as no departure is made from the main point of the invention. In the working examples, "parts" means "parts by weight." The property values in the working examples were measured as follows.

· Intrinsic viscosity [ $\eta$ ]

Calculated from the solution viscosity measured at 35°C using a phenol/tetrachloroethane (ratio: 3/2) solvent.

· Transmitted light intensity ( $T_{400}$  and  $T_{420}$ ) at wavelengths of 400 nm and 420 nm

A quantity of 0.25 g of polyethylene naphthalate was dissolved in a 2:3 mixed solvent of hexafluoroisopropanol and chloroform. After adjustment to 25 mL of solution (10 mg/mL), the transmittance at 400 nm and 420 nm ( $T_{400}$  and  $T_{420}$ , unit: %/cm) was measured by an automated spectrophotometer UV-3101P made by Shimadzu.

· Heat stability

The heat deterioration index was determined using the following formula from the intrinsic viscosity of the polymer before and after molding a preform, and the heat stability of the polymer was evaluated.

$$\text{Heat deterioration index} = ([\eta_0]/[\eta_x])-1$$

Where,  $[\eta_0]$ : Intrinsic viscosity of polymer before producing preform

$[\eta_x]$ : Intrinsic viscosity of molded preform

Evaluation criteria	Heat deterioration index $\leq 0.05$	Heat stability ○
	$0.05 < \text{heat deterioration index} \leq 0.10$	Heat stability △
	$0.10 < \text{heat deterioration index}$	Heat stability ×

· Cal (hue)

Polymer pellets were heat treated for 90 minutes in a dryer at 160°C. After crystallization, they were measured by a CM-7500 color machine (Color Machine).

· Bottle haze: After being dried for 7 hours at 160°C, the polymer was molded into a 50 g preform at a cylinder temperature of 300°C using an injection molding machine (Dynamelter M-100DM; Meiki Seisakusho). This preform was blow stretched and made into a bottle with an internal capacity of 1.5 L and a body thickness of 0.2 mm. The body was cut from the bottle, and the haze was measured using a haze meter (1001DP, Nippon Denshoku).

[0023] [Working Example 1] One hundred parts of dimethyl 2,6-naphthalene dicarboxylate and 60 parts of ethylene glycol were transesterified by the usual method using 0.03 part (1.23 mol) of

manganese acetate tetrahydrate as the transesterification catalyst. A quantity of 0.023 part (1.64 mol) of trimethyl phosphate was then added and transesterification was substantially ended.

[0024] Next, after adding 0.049 part (1.64 mol) of antimony acetate, polycondensation was carried out by the usual method under high temperature and high vacuum. Strand-shaped chips were obtained thereafter by ejecting the product into a large amount of running water by the usual method. The target  $[\eta]$  of the polymer obtained is 0.60. It took 110 minutes of polymerization to reach it.

[0025] [Working Examples 2-7 and Comparative Examples 1-6] These examples were basically the same as Working Example 1 except that the amounts and proportions of magnesium [sic] acetate tetrahydrate, trimethyl phosphate, and antimony acetate or antimony trioxide were as shown in Table 1.

[0026] The quality and results of evaluation of the polymers obtained are also shown in Table 1.

[Table 1]

	Amount of catalyst (mol) <sup>*1</sup>			Catalyst ratio Mn/P	Polymerization time (min)	[η]	ε <sub>0</sub> L/b	T <sub>400</sub> %	ΔT %	Heat stability	Bottle haze (%)
	Mn	P	Sb								
Working example 1	1.23	1.64	Sb(oAc) <sub>3</sub> = 1.64	0.75	110	0.60	70/3.0	97.8	1.8	○	0.9
Working example 2	0.80	1.07	Sb(oAc) <sub>3</sub> = 1.64	0.75	120	0.60	71/3.2	98.0	1.5	○	0.8
Working example 3	1.60	2.13	Sb(oAc) <sub>3</sub> = 1.64	0.75	110	0.60	71/3.3	97.2	2.0	○	1.1
Working example 4	1.23	1.12	Sb(oAc) <sub>3</sub> = 1.64	1.10	115	0.60	70/2.5	96.5	2.1	○	1.2
Working example 5	1.23	1.64	Sb(oAc) <sub>3</sub> = 2.46	0.75	105	0.60	68/2.8	96.0	2.3	○	1.3
Working example 6	1.23	1.64	Sb <sub>2</sub> O <sub>3</sub> = 1.64	0.75	110	0.60	68/3.8	96.0	2.0	○	1.2
Working example 7	1.23	1.89	Sb <sub>2</sub> O <sub>3</sub> = 1.64	0.65	125	0.60	67/3.9	95.7	2.1	○	1.3
Comparative example 1	1.84	2.46	Sb(oAc) <sub>3</sub> = 1.64	0.75	110	0.60	68/4.0	94.8	3.1	△	1.7
Comparative example 2	0.65	0.87	Sb(oAc) <sub>3</sub> = 1.64	0.75	180 (cut off)	0.50	65/4.5	93.1	1.7	○	Poor molding
Comparative example 3	1.23	2.50	Sb(oAc) <sub>3</sub> = 1.64	0.49	120	0.60	68/2.9	92.0	1.5	×	2.0
Comparative example 4	1.23	0.82	Sb(oAc) <sub>3</sub> = 1.64	1.50	115	0.60	69/4.8	96.5	3.7	×	1.6
Comparative example 5	1.23	1.64	Sb(oAc) <sub>3</sub> = 3.28	0.75	95	0.60	63/2.9	92.8	3.6	△	1.9
Comparative example 6	1.23	1.64	Sb <sub>2</sub> O <sub>3</sub> = 0.95	0.75	180 (cut off)	0.57	72/4.1	97.0	2.4	○	2.1

\*1) Number of moles per 10<sup>6</sup> g of acid component

[0028] According to these results, the reactivity is poor and problems arise in productivity when the amount of catalyst is too small (Comparative Examples 2 and 6). Conversely, when too large an amount of catalyst is used (Comparative Examples 1 and 5) or when the Mn/P ratio is not proper (Comparative Examples 3 and 4), the hue (transmittance) deteriorates and the bottle turns white during molding.

[0029]

**[Effect of the Invention]** The polyethylene naphthalate of the present invention has excellent heat stability, hue, and transparency, does not turn white (cloud) during bottle molding, and makes it possible to obtain molded bottles of high product value.